Studies in qualitative Organic Analysis

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STUDIES IN QUALITATIVE ORGANIC ANALYSIS

BY

SIDNEY DALE KIRKPATRICK

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

SIDNEY DALE KIRKPATRICK

ENTITLED   STUDIES IN QUALITATIVE ORGANIC ANALYSIS

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF___ BACHELOR OF SCIENCE

C. G. Derick
Instructor in Charge

APPROVED: *W. A. Noyes*

HEAD OF DEPARTMENT OF *Chemistry*

STUDIES IN QUALITATIVE ORGANIC ANALYSIS

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STUDIES

IN

QUALITATIVE ORGANIC ANALYSIS

Introduction

The purpose of this work has been to study somewhat in detail three problems which are concerned in qualitative organic analysis. While the divisions of the subject are not closely related each to each, there exists, nevertheless, a definite correlation between them and the general and comprehensive scheme which has been developed for the separation and identification of organic compounds. From the enormous number of these compounds and from the fact that some of them are of marked instability while others differ only slightly in their chemical and physical properties, it will be seen that this system can never be worked out with the same degree of certainty and completeness which is evidenced in the case of the common inorganic compounds. Nevertheless, a number of satisfactory schemes are now in use. One of the most practical methods that has been developed has been to divide all organic substances into groups based upon the relative solubility they show toward a few selected solvents. The compounds of these groups are further divided into their homologous series by means of what are known as homologous tests. These tests take advantage of the generalization that the chemical properties of each of the compounds in a series are closely similar, while their physical characteristics usually differ widely. Final-

ly the individuals of the series are identified by the determination of their physical constants, by the use of some specific reaction characteristic to the individual, or by the preparation of easily characterized derivatives.

The first part of this work has been concerned with the development of one of these homologous tests mentioned above; namely, the use of dimethyl sulphate as a qualitative method of separating the aromatic hydro-carbons from those of the saturated aliphatic or paraffin series. This separation is most commonly made with fuming sulphuric acid and because of the danger involved in the technique and the inconvenience occurred in the recovery of the dissolved hydrocarbons, this method has not been entirely satisfactory for general use.

The second part takes up the recovery from solution of those compounds which are soluble in cold concentrated sulphuric acid. This reagent is used in the group division which is called the indifferent group, which contains all of those substances which are insoluble in water, dilute alkali, or dilute acid. With the exception of the hydrocarbons and most of their halogen substitution products, all of the homologous series present in this group are soluble in cold concentrated sulphuric acid, and this work is but a study of how comprehensively these compounds, alone or in mixtures, may be recovered from their solution in this acid.

The third part of the work, which is probably the least closely related to the systematic analytical classification, has consisted of a study of the equilibrium in the Friedel and Crafts' reaction. This reaction, along with a number of other similar syntheses, is often mentioned in text books* of qualitative

* F. E. Weston: "A Scheme for the Detection of the More Common Classes of Carbon Compounds."

organic analysis as being a characteristic reaction which might be applied qualitatively as tests for certain classes of compounds. In very few cases are there specified the laboratory conditions, mass relations, or product yields,- all of which must be known if the reaction is to fit into the general analytical scheme. This particular reaction, as is the case with many of those sometimes cited, is not entirely practical when carried on in the test tube quantities of the usual qualitative test. This study of the equilibrium has been made rather with the hope that with the data obtained, - after having stated definitely the laboratory conditions and mass relations of the experiment,- it will be possible to predict the yield of the product or rather the proportion of the different products formed by the reaction.

I.

DIMETHYL SULPHATE: ITS USE AS A MEANS OF QUALITATIVELY
SEPARATING THE AROMATIC HYDROCARBONS FROM THOSE OF THE
PARAFFIN SERIES.

Historical Part.

The use of dimethyl sulphate in the separation of hydrocarbons
was first proposed by E. Valenta in 1906.[1] He found that this
reagent dissolved aromatic hydrocarbons, such as occur in coal tar,
in all proportions while it neither dissolved nor was soluble in
the hydrocarbons of the paraffin series such as the mineral and
rosin oils. Consequently the quantity of coal tar oils added to
either of these oils might be rapidly determined by simply shaking
up the sample in a stoppered measuring cylinder and noting the
increase in the volume of the dimethyl sulphate. Valenta further
claimed that the separation could be made with an accuracy of one
or at most two per cent. Accordingly, it would appear that he
had discovered a quantitative method of estimating the aromatic
or tar oils which at that time were often used to adulterate
the aliphatic or mineral oils. Also since dimethyl sulphate dis-
solves such substances as nitrobenzene, nitronaphthalene, etc.
which are used as deblooming agents for mineral oils, the method
would be of further commercial importance in the extraction and
estimation of these materials.

The next investigation was the work of E. Graefe,[2] who in 1907
showed that in the case of mixtures of hydrocarbons of low boil-
ing point, the composition of the mixture could not be inferred
solely from the dimethyl sulphate test. The reason for this was

(1) E. Valenta. Chem. Zeit. XXX. 266 (1906)
(2) E. Graefe. Analyst, 32: 225, (1907)

that, on the one hand, aliphatic hydrocarbons are not absolutely
insoluble in this solvent; and, on the other hand, the aromatic
hydrocarbons that dissolve appear to increase the solvent action
of the dimethyl sulphate upon the aliphatic hydrocarbons. Further
he finds that the error which Valenta had estimated at one per
cent amounts usually to more than ten per cent, but that the
apparently regular increase observed in the difference between the
theoretical and actual amounts soluble in one and one-half volumes
of dimethyl sulphate, would seem to show that the method had some
value in the examination of even the hydrocarbons of low boiling
point. In the case of the distillates of medium boilingpoint,
Graefe found that the test gave good results which were only
slightly affected even by a high proportion of aromatic hydro-
carbons in the mixture.

These findings of Graefe finally led to a more exhaustive inves-
tigation by the Analytical Association of England, the results of
their work being published in 1908 by Harrison and Perkin.[3] These
men disagree with Valenta's original contentions, having found
the mineral oils to be soluble to quite an appreciable extent;
for example, petroleum ether, when shaken with one and one-half
volumes of the sulphate, showed a solubility of over seventeen
per cent. They obtained a considerable amount of data working
with the different hydrocarbons separately and with them in mix-
tures of varying proportions. The investigation also included a
number of the trade oils referred to by Valenta, but from the
results obtained with them and with the hydrocarbon mixtures, they
concluded that his claims could not be substantiated and his method
could not be recommended for quantitative estimation.

(3) Harrison and Perkin, Analyst, 33: 2-11. (1908.

Dimethyl sulphate is a colorless, oily liquid which boils at 188.3°-188.6°C., and has a specific gravity of 1.3334 at 15°C. [4] It was first prepared in 1835 by J. Dumas and E. Peligot, who distilled methyl alcohol with 8-10 parts of concentrated sulphuric acid. The reagent has a slight odor of sulphurous acid and is reputed to have toxic properties. In these tests the dimethyl sulphate is always used at atmospheric temperatures and the danger of inhaling the vapors is thus lessened considerably. The convenience with which it may be used and its moderate cost makes possible a general and practical application as a reagent.

Theoretical Part.

The theory of the mechanism of the dissolving action of the dimethyl sulphate upon the aromatic hydrocarbons has not as yet been worked out. On the one hand, there appears to be some evidence that the action is purely one of solution, while, on the other hand, some of the investigations made by the writer would seem to indicate that a compound, probably of additive nature, is formed between the hydrocarbon and the dimethyl sulphate. With paraffin hydrocarbons alone it has been noted that the sulphate has but a slight dissolving action. Also Graefe's statement that the aromatic hydrocarbons which dissolve increase the solvent action of the dimethyl sulphate upon the paraffins has been confirmed by experimental data. A simple explanation of this is the fact that the paraffin hydrocarbons are soluble in all proportions in the aromatic and the amounts dissolved from a mixture will naturally increase with the increasing proportion of the aromatic hydrocarbon present.

(4) J. Dumas and E. Peligot. Annalen der Pharmacie, 15: 40 (1835)

The questionof whether or not a compound is formed is brought up only as a possible explanation of the fact that unsaturated hydrocarbons dissolve, whereas, the paraffins do not. The method used in detecting the presence of a compound was by the construction of a temperature-composition diagram for the two-component system, benzene-dimethyl sulphate, using the method of "thermal analysis," which is based upon the character of the cooling curves obtained with liquid mixtures of varying compositions. From this diagram,(included with the experimental work of the report) it will be observed that a compound with roughly the proportions of one mole benzene to three moles of dimethyl sulphate is probably formed.

<center>Experimental Part.</center>

Solubility of Paraffin Hydrocarbons:

Samples of ligroin and kerosene were fractionally distilled in order to obtain the different fractions which were to be studied, namely those between 30-50, 50-100, 100-150, 150-200, 20-250, and 250-300 degrees Centigrade. Before distilling, the materials were purified by shaking first with fuming sulphuric acid to remove any aromatic or unsaturated aliphatic constituents, then with dilute potassium hydroxide, and finally washed with water and dried. The fractions were treated with equal volumes of dimethyl sulphate by shaking for three minutes in a graduated separatory funnel. They were then allowed to stand until a clear line of separation between the liquids would appear- a process which usually required only a minute or so after the shaking. The results obtained were as follows:

Fraction	Temperature Deg. C.	Volume in c.c.before Treatment	Volume in c.c. after Treatment.
1	30 - 50	2	2
2	50 - 100	10	9.4
3	100 - 150	13.5	13.0
4	150 - 200	19.0	19.0
5	200 - 250	23.5	23.5
6	250 - 300	14.0	14.0

Further examination of the ligroin fractions between 50°- 100° showed that the maximum solvent action was evident in the ten degree fraction, 50-60°.

Normal heptane, the Kahlbaum product which had been especially purified by distillation and treatment with fuming sulphuric acid as mentioned above, was next tested. A twenty c.c. quantity of the hydrocarbon was shaken in the graduated separatory funnel first with an equal volume , and then with one and one-half times its volume of dimethyl sulphate. In neither case was there any appreciable quantity dissolved. (only a fraction of one c.c).

A sample of cyclo-hexane, which had been prepared by the hydrogenation of benzene, was purified with fuming sulphuric acid, tested with dimethyl sulphate, and found to be insoluble. Solubility of Halogen Substitution Products of Hydrocarbons, (and a few other compounds.)   These samples were taken from the laboratory collection and treated with equal volumes of dimethyl sulphate without further purifcation.   The results were as follows

      1. Chloroform   Soluble completely

      2. Amyl chloride   "

      3. Dichlorobromethane   "

4. Isobutyl bromide	Soluble completely	
5. Propylene bromide	"	"
6. Chlortoluol	"	"
7. Propyl iodide	Soluble in 2-1/2 volumes	
8. Bromobenzene	Slowly soluble	
9. Chlorobenzene	Soluble completely	
10. Ethyl bromide	"	"
11. Allyl bromide	Soluble in 2-1/2 volumes	
12. Amylene	Soluble completely	
13. Naphthalene	"	"
14. Diphenyl	Soluble slowly in 2 volumes	
15. Benzyl benzoic ester	Soluble completely	

Solubilities in Mixtures of Hydrocarbons:

The first mixtures investigated were made up of equal volumes
of toluol and normal heptane. Both materials were carefully
purified, the paraffin by the method previously described, while
the aromatic hydrocarbon was shaken successively with cold con-
centrated sulphuric acid, dilute alkali, and water. After drying
over calcium chloride, 25 c.c. of each were mixed and shaken for
three minutes with 30 c.c. of dimethyl sulphate. The undissolved
portion which amounted to 33 c.c. was then given a second
application of the dimethyl sulphate, which diminished the volume
to 25 c.c. This, on shaking with fuming sulphuric acid, proved
to contain 20 c.c. of the original heptane.

The solvent action of the aromatic hydrocarbon when dissolved
in the dimethyl sulphate was demonstrated by the use of the two
mixtures of somewhat extreme proportions. In the first case, with

20 cc. of heptane to 5 cc. of benzene, two applications of dimethyl
sulphate decreased the volume only to 21 cc., and this, on shak-
ing with fuming sulphuric acid, yielded the original amount of
heptane still undissolved. The second mixture of the proportions
5 cc. of heptane to 20 cc of benzene, was shaken with 20 cc. of
dimethyl sulphate, and it was observed that on the first treatment
the undissolved remainder had decreased to less than one cc.
From these mixtures it is seen that the solvent action depends
somewhat upon the benzene present, for in the first mixture where
the "benzene in dimethyl sulphate" was dilute, there was no
appreciable dissolving. On the other hand, in the second mixture,
where the benzene was in excess, all of the heptane was dissolved
by the "benzene in dimethyl sulphate solution."

Recovery of the Dissolved Hydrocarbon:

The dissolved hydrocarbons may be recovered from their
solution in dimethyl sulphate by saponification. The sulphate
when taken alone is easily saponified by refluxing with 20% KOH
for three minutes, but when some of the hydrocarbons are dissolved
in it, slightly greater difficulty is experienced. This is due
for the most part to the bumping of the boiling mixture in the
flask in which the refluxing is carried on. A more convenient
method of recovery, which has proven entirely satisfactory, has
been to reflux the mixture for a short time with alcoholic KOH
and recovering the hydrocarbon from the emulsion by extracting
with ether.

Temperature-constitution Diagram for Benzene-Dimethyl Sulphate:

In order to obtain the necessary data for a temperature-
constitution diagram, a series of eleven mixtures of benzene and

dimethyl sulphate were made up in proportions varying from pure benzene at the one extreme to pure dimethyl sulphate at the other. The freezing point of each of these mixtures was determined by constructing a cooling curve or temperature-time diagram. The temperatures were measured by means of a copper-constantin thermo-couple and milli-voltmeter, which had been calibrated for two points, namely, the freezing points of water and of mercury. The procedure was as follows: The mixture being studied was placed in a teat tube, the junction of the termo-couple fastened securely within the center of the tube, and the whole was placed in a Dewar bulb containing the freezing mixture of solid carbon dioxide and ether. After the mixture had completely frozen, the tube was removed, and after drying the condensed moisture from the outside, was placed in a larger tube which was tightly stoppered. This was done in order to prevent the moisture from collecting on the outside of the tube containing the mixture, and thus interfering with the thermal effect. Immediately after placing into the larger tube, the temperatures were read at ten second intervals until the solid had entirely melted. From the data obtained in this way, a cooling curve was plotted and the freezing point for the mixture was taken from this curve. This was repeated for each of the mixtures and the values so obtained were used to construct the accompanying temperature-constitution diagram. From this diagram it is observed that a compound is formed which melts at -47°C. and has a composition of approximately 80% of dimethyl sulphate and 20% of benzene.

<center>Conclusions: Summary of Part I.</center>

1. Dimethyl sulphate, while it cannot be used quantitatively, offers a means of separating aromatic and paraffin hydrocarbons

-11a-

TEMPERATURE - CONSTITUTION DIAGRAM

FOR THE SYSTEM

BENZENE - DIMETHYL SULPHATE
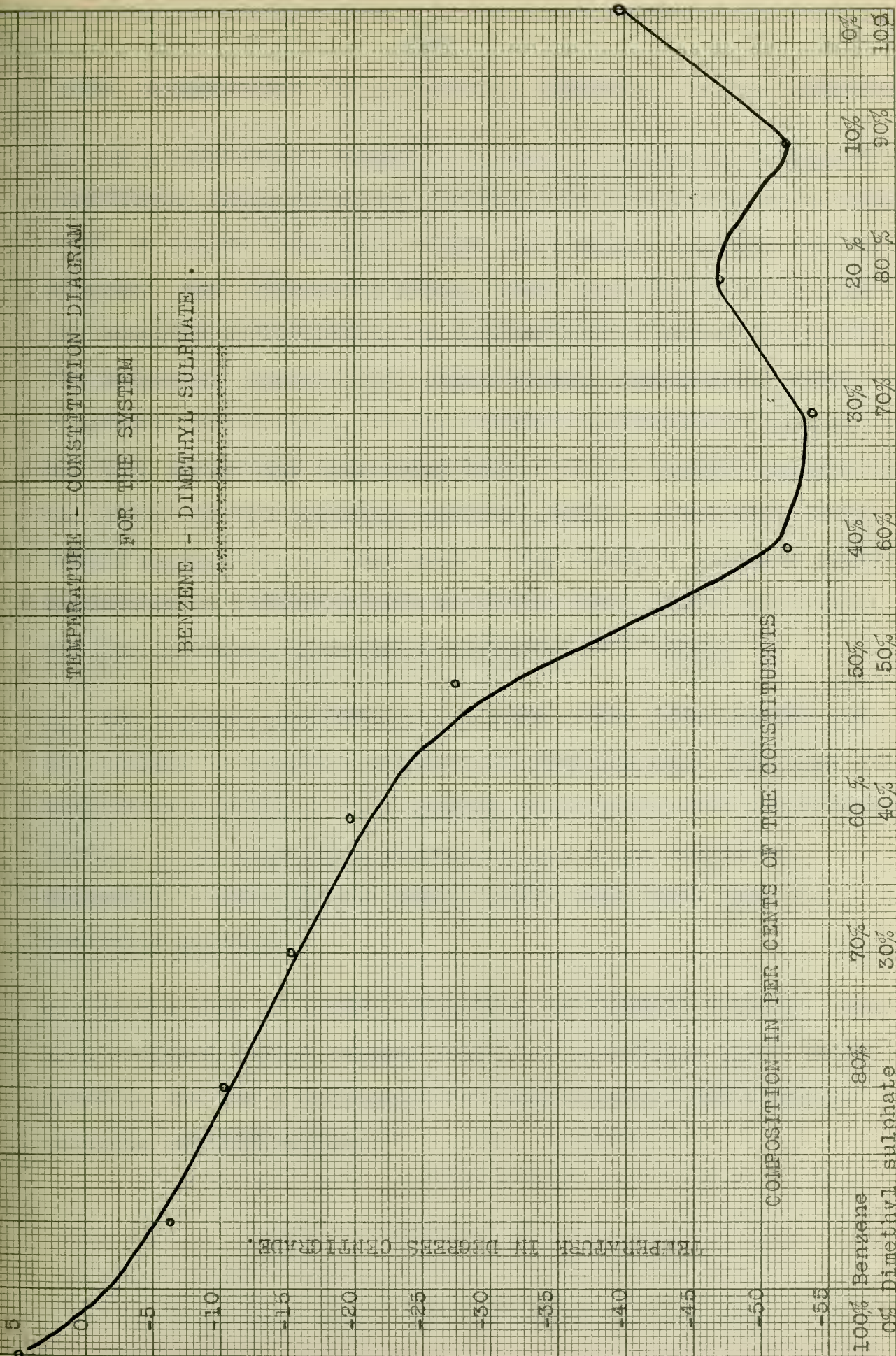
which is applicable for qualitative separation in the laboratory.

2. As a qualitative method: A mixture of those substances of the Indifferent Group which are insoluble in cold concentrated sulphuric acid, is shaken with equal volume of dimethyl sulphate for three minutes. The undissolved layer, which may still contain some of the aromatic hydrocarbons, is treated with a second application of the sulphate. The solvent action of this second application is limited almost entirely to the aromatic hydrocarbons because as has been shown, the dissolving action of the reagent depends upon the amount of the dissolved aromatic, which in the case of the second application is very small. The dimethyl sulphate layer is saponified by refluxing with alcoholic KOH, diluted with water, and the recovered hydrocarbon extracted with ether.

3. The halogen substitution products of the hydrocarbons are all soluble in dimethyl sulphate so that the fact that part of a mixture is soluble in this reagent is no proof that the dissolved portion is an aromatic hydrocarbon, and it is therefore necessary to saponify and employ additional tests upon the recovered product.

4. In the case of benzene dissolved in dimethyl sulphate, there is a compound formed between these two substances which melts at -47°C. and has a composition of approximately 80% dimethyl sulphate and 20% benzene.

II.

RECOVERY FROM SOLUTION OF THOSE COMPOUNDS WHICH ARE
SOLUBLE IN COLD CONCENTRATED SULPHURIC ACID.

(5)
In the scheme of qualitative organic analysis, which has
been satisfactorily developed within the last few years at the
University of Illinois,--cold concentrated sulphuric acid plays
a very important role'. As mentioned in the introduction of this
paper, it is one of the four selected solvents, which are used
ih the classifying of all organic compounds into three large
groups. The first division includes all of the compounds which
are soluble in water and it is further divided under the two
heads, Ether Soluble and Ether Insoluble. The second part of the
classification contains the organic substances which are insoluble
in water but which are dissolved by either dilute acid or dilute
alkali. In further division, those compounds dissolved by the
first reagent make up the Basic Substances while the alkali
soluble compounds form the Acidic Substances. The nature and con-
centration of the alkali and acid as well as the temperature at
which they are used, are of course essential in this method of
classification. All compounds not falling under any of the
above headings are classified in the Indifferent Division.
Accordingly, this division contains all organic compounds which
are insoluble in water, dilute HCl, or dilute KOH.

The solvent used for the further sub-division of this
group is cold concentrated sulphuric acid, which offers the
following classification:

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(5) Qualitative Org. Anal. (Mimeographed outline used at Univ.ofIll
C. G. Derick.

INDIFFERENT COMPOUNDS.

That is, Insol. in H_2O, dil. HCl, or dil. KOH.

GROUP "A"   GROUP "B"

Sol. in Cold Con. H_2SO_4 Insol. in Cold Con. H_2SO_4

1. Alcohols (high molecular wgt.   1. Aliphatic saturated hydro-
                                       carbons.
2. Aldehydes   "   "   "
                                    2. Aromatic hydrocarbons
3. Ketones   "   " "   "
                                    3. Halogen substitution prod-
4. Ethers   "   "   "   ucts of above.

5. Acid Halides"   "   "

6. Anhydrides   "   "   "

7. Unsaturated Hydrocarbons

8. Esters and Lactones

9. Amides(Including negatively
     substituted amines.)

10. Nitriles

11. Tertiary Nitro compounds

12. Various Sulphur compounds

Note: There are some few of the halogen substitution prod-
ucts of the hydrocarbons which do dissolve (with decomposition)
in the sulphuric acid. This is particularly true of the
aliphatic compounds where the halogen is on a tertiary carbon
atom, or the aromatic, in which the halogen is on the first
carbon atom of the side chain.

By the use of the Dimethyl Sulphate test as developed in the
first part of this investigation, a means is offered of subdivid-
ing Group B and separating the hydrocarbons of the paraffin series
from the other two classes of insoluble compounds. Now it is
hoped to further develop the values of these tests by offering a
sub-division to Group A, whereby certain of the classes of com-
pounds, which can be recovered from their solution in sulphuric

acid by dilution methods, may be separated from those which can not be so recovered.

Attention was called to the possibility of dividing the group in some such manner as this, by the "Ether Test"[6] given by Professor S. P. Mulliken in his text on Qualitative organic analysis. He points out that if the saturated ethers are dissolved in ice cold sulphuric acid (sp. gr. 1.84) and dilution made by pouring into ice water, the original ethers can be recovered almost quantiatively. Somewhat the same procedure as he has outlined for the ethers has been applied to the other classes of compounds of Group A. In this work an effort has been made to study as large a number as possible of representative compounds so chosen as to cover all of the types which make up the group.

EXPERIMENTAL WORK.

The first work done was with the alcohols of high molecular weight and a number of typical compounds were investigated. Those which fall on the border line between the water soluble and indifferent groups were first studied. It was found that it was impossible to obtain satisfactory results with isobutyl alcohol, while amyl alcohol which is next in the series could be recovered to a considerable extent providing particular care was exercised in making the dilutions. For instance in a typical experiment with this compound, to 5 cc of the alcohol in a test tube there was added 10 cc. of ice cold concentrated sulphuric acid. After shaking to produce a clear yellow solution, the contents of the tube were poured into 30 cc. of ice water and the separation into two layers resulted. The upper layer, after washing with a

[6] A Method of Identification of Pure Organic Compounds. S.P. Mulliken. Vol. I, page 199-201.

small quantity of water and drying over fused potassium carbonate,
amounted to 3 c.c. This was identified as the original alcohol
by a boiling point determination. The next part of the work was
with the higher alcohols,(those having more than 5 carbon atoms)
where it was found that recovery could be made on almost a
quantitative basis.

Aldehydes of high molecular weight dissolve in cold concen-
trated sulphuric acid, but for the most part the solution takes
place with decomposition. For this reason attempts at recovery
by dilution methods were unsuccessful with the compounds investi-
gated. Benzaldehyde is decomposed and yields benzoic acid as one
of the products. Other aldehydes of higher molecular weight such
as vanillin and piperonal acted similarly.

The heavy ketones, on the other hand, may be readily re-
covered by this method. A number of satisfactory experiments were
made with acetophenone and with methyl propyl ketone. Even better
results were obtained with gamma keto alpha phenyl butane, a
ketone of considerably higher molecular weight.

In the case of the saturated ethers positive results were
obtained, as might be expected from the fact that the test was
originally developed for ether recovery. It was found that even
ethyl ether could be recovered on a basis sufficiently accurate
for practical qualitative work. There was only one exception
noted and that was methylal, which dissolved readily in the acid
but could not be recovered by dilution. This behavior is no
doubt due to the fact that methyal is soluble in water in the
ratio of almost 30 parts in 100.

The esters of high molecular weight could also be satis-

factorily recovered, but here, too, there was one exception.
Benzyl benzoate is decomposed by the action of the sulphuric acid
and yields a white precipitate of benzoic acid as one of its de-
composition products. The other esters studied, such as methyl
benzoate, ethyl benzoate, isoamyl benzoate, ethyl phenyl acetate,
and ethyl malonate, were easily recovered and the results were
practically quantitative.

The acid halides, anhydrides, and the unsaturated hydro-
carbons could not be recovered as they were acted upon by the acid.
Also in the case of the amides and negatively substituted amines,
the method does not seem to be of very practical importance. It
has been found that the most of these compounds are so difficultly
soluble in the sulphuric acid, that if they were present in any
large quantity, they would interfere appreciably with any separa-
tion carried out with this reagent.* The data obtained from the
experiments with acetanilid, benzamide, carbamide, succinamide,
phthalamide and phthalimide, would not warrant the recommendation
of the recovery method for this class of compounds.

However, in the case of the nitriles, the opposite seems to
be true. Benzonitrile, propionitrile, p. tolyl nitrile, and sever-
al others could be recovered from their solution in sulphuric acid
almost quantitatively. Practical application of this was made by
Hess [7] in purifying a compound $BrCH_2CH_2CH_2C\equiv N$ which was mixed with
the dibromide, $BrCH_2CH_2CH_2Br$. On shaking with ice cold concen-

(*)These compounds are exactly those which would be detected by the
   elementary analysis and so would not be confused with the in-
   soluble hydrocarbons.
(7) R. W. Hess. Ph.D.Thesis, 1916. University of Illinois.

trated sulphuric acid, all of the nitrile present went into
solution, while the dibromide compound remained undissolved. On
pouring the sulphuric acid solution into ice water, he was able
to recover all of the nitrile.

Tertiary nitro compounds are all soluble and are readily
recovered from their solution. This was demonstrated with such
typical compounds as nitrobenzol, and the mono, di-,and tri-nitro-
toluoles.

Conclusions: Summary of Part II.

1. The recovery of the substances which are dissolved by cold
concentrated sulphuric acid is not limited entirely to the satura-
ted ethers, but may be applied to many other of the different
classes of compounds belonging to the soluble division of the
Indifferent Group.

2. A means is afforded of dividing the soluble constituents of
the Indifferent Group into two divisions; the first containing those
classes of compounds which may be recovered from their solution
in cold concentrated sulphuric acid by dilution with ice water,
while the second division contains those classes which cannot be
so recovered. From the data obtained, the division is as follows:

GROUP "A"

Soluble in cold concentrated Sulphuric acid.

| Sub-Group I (Recovered by Dilution)	Sub-Group II (Not Recovered)
1. Alcohols (high molecular weight)	1. Aldehydes (High Mol.wgt.
2. Ketones " " "	2. Acid Halides " " "
3. Ethers " " "	3. " Anhydrides
4. Esters	4. Unsaturated Hydrocarbons
5. Nitriles	5. Amides(Including Nega-
6. III Nitro compounds.	tively substi-
	tuted amines.)

III.

A STUDY OF THE EQUILIBRIUM OF THE FRIEDEL AND CRAFTS' REACTION.

Historical Part.

The Friedel and Crafts' reaction, which is one of the oldest and most familiar reactions of organic chemistry, was discovered in 1877 by C. Friedel and J. M. Crafts. (British patent No. 4769). In their first published work,[8] they demonstrated that, in the presence of the chloride, iodide, or bromide of aluminium, an organic halide would react with a hydrocarbon of the benzene series in such a manner that the halogen would combine with a hydrogen atom of the hydrocarbon and would be liberated as the halogen acid, while the alkyl group would replace this hydrogen and form as a result the substituted hydrocarbon. The paper took up for the most part the synthesis of a number of hydrocarbons, preparing such compounds as amyl benzene, ethyl benzene, toluene, xylene, mesitylene, penta-and hexa-methyl benzene, and tri-phenyl methane. It was also pointed out that the reaction was not limited merely to the synthesis of the hydrocarbons, but for example, it was demonstrated that a ketone, such as benzophenone, could be prepared by the action of benzoyl chloride upon benzene in the presence of aluminium chloride.

To explain these changes, the authors assumed the formation of an intermediate product, $C_6H_5Al_2Cl_5$ which would react with the alkyl halide regenerating the aluminium chloride.

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(8) Friedel and Crafts. Compt. rend. <u>84</u>: 1392. (1877)

$$C_6H_5Al_2Cl_5 + C_2H_5Cl = C_6H_5C_2H_5 + 2Al\,Cl_3$$
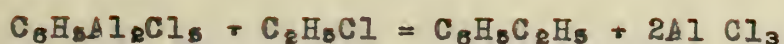
According to this reaction, the aluminium chloride acts in the capacity of a true catalyst. The fact that a small quantity of the reagent will not bring about the union of an indefinite amount of the reacting materials, but is actually used up in the reaction, has given rise to a number of theories concerning the mechanism of the reaction. Nevertheless, the original idea of an intermediate product has been borne out by the work of a number of investigators[9], and compounds, although perhaps of not exactly the composition assumed by Friedel and Crafts, have been definitely isolated. Steele[10], one of the more recent investigators, concludes "that the action of the aluminium and ferric chlorides in inducing the Friedel and Crafts' reaction, differs from many cases of true catalysis only in the accident that these reagents combine with certain substances produced during the reaction and are thus removed from the system."

Friedel and Crafts, in their next paper[11], discussed the decomposing action of aluminium chloride upon the hydrocarbons. For example when benzene is treated with aluminium chloride it will yield toluene and ethyl benzene together with diphenyl. Here it would seem that in the reaction, there was a certain number of benzene molecules which were broken down to form methyl and ethyl groupings, while at the same time there was an interchange of hydrogen for phenyl.

R. Anschutz and H. Immendorfer[12], also working along this line, showed that by the action of aluminium chloride upon toluene,

(9) Gustavson. Berichte 11:2151, (1878)
(10) Steele. Trans. Chem. Soc. 83: 1470, (1903)
(11) Friedel and Crafts. Ann. Chim.Phy. (6) 14: 433-72 (1888)

both benzene and xylene were formed; while in the same way xylene
was found to yield benzene, toluene, and mesitylene; and ethyl
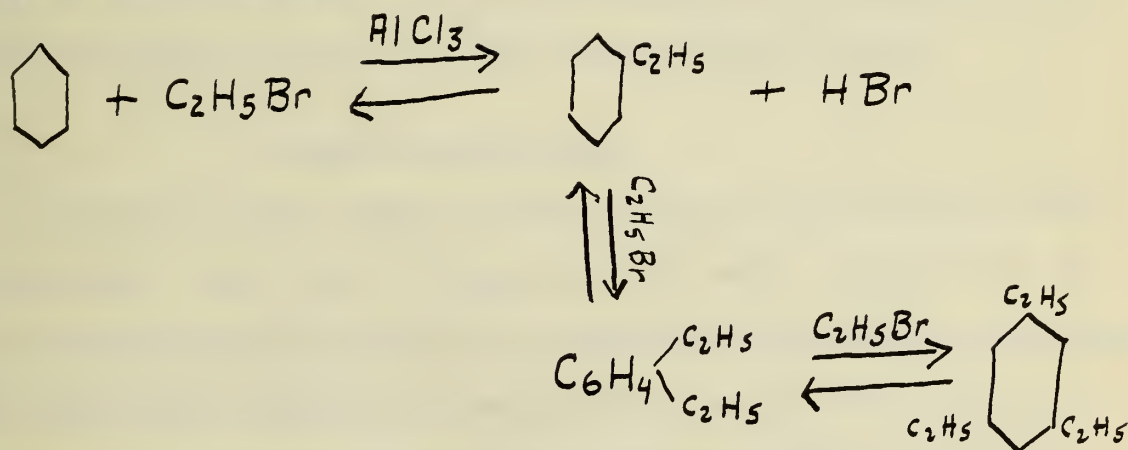benzene gave benzene and diethyl benzene.

(13)

C. Radzuwanowski was the first to apply these principles
to a study of the reaction from the synthetic point of view. In
a typical reaction such as the preparation of ethyl benzene, he
observed that a large part of the active radicle was lost. For
example, with 7 parts of ethyl bromide and 10.5 parts of benzene
only 33% of the theoretical yield of ethyl benzene was obtained,
while the ethyl radicle corresponding to the other 67% was lost.
Since in the reaction there was always formed a considerable
quantity of the di- and tri-ethyl benzenes, Radzuwanski was able
to demonstrate that the yield of the mono-ethyl benzene might
be increased by the destruction of these higher boiling products
by means of the decomposing action of aluminium chloride. In the
case of the ethyl benzene, he was able to increase the yield of
the desired product from 33% to 71.% In the preparation of di-
phenyl methane by the Friedel and Crafts' reaction, he observed
that there was considerably less loss, being able to obtain a
56% yield. Using the same procedure as with ethyl benzene, namely
boiling the higher boiling products with aluminium chloride in
benzene solution, he was able to increase the yield materially,
and instead of 56% he obtained 83% of the theoretical yield of
diphenyl methane.

Theoretical Part.

For the purpose of this study, the ethyl benzene synthesis
was chosen as representing one of the most characteristic examples

(13) C. Radzuwanski. Berichte, 27 : 3235-37. (1894)

of the Friedel and Crafts' reaction. Ethyl bromide and benzene in
the presence of aluminium chloride give ethyl benzene and a some-
what smaller proportion of the di- and tri- ethyl benzenes. The
reaction represents an equilibrium or rather a series of equilibria
between these products. The fact that alkyl groups can either be
substituted onto the phenyl ring or can be removed from it, as was
demonstrated in the work already cited, would seem to indicate
that the reaction was of an equilibrium nature,-- and the results
of the work in this parficular study of the reaction have definitely
proven this to be true. The chemical equations representing this
reaction may be stated as below: but at present, there is no
definite evidence to show that the equilibria is between just the
substances here indicated.

$$\bigcirc + C_2H_5Br \underset{\longleftarrow}{\overset{AlCl_3}{\longrightarrow}} \bigcirc C_2H_5 + HBr$$

$$\updownarrow C_2H_5Br$$

$$C_6H_4 \Big\langle {C_2H_5 \atop C_2H_5} \underset{C_2H_5}{\overset{C_2H_5Br}{\underset{\longleftarrow}{\longrightarrow}}} \overset{C_2H_5}{\bigcirc} {C_2H_5 \atop C_2H_5}$$

In this work a very simple method was used to demonstrate
the presence of the equilibrium. After having decided upon the
factors which were most likely to bring about equilibrium conditims,
 a synthesis was made.and the proportion of the different products
was determined. The products were then poured together again and
another treatment with aluminium chloride made, after which the
various products were separated for the second time. If now the

proportion of these checked with the original quantities, it was assumed that equilibrium had been reached. Then, instead of returning all of the products for another application of aluminium chloride, a part of one was held back, thus varying the proportion of one of the reacting materials. The equilibrium would then be shifted, but on adding the remainder of the product withheld, and again treating with aluminium chloride, the original proportion of the products under the equilibrum conditions would be reattained.

In this way by maintaining constant all of the factors effecting the equilibrum with the exception of the one whose effect was being studied, it was possible to shift the equilibrium in either direction desired and thus determine the proportion of the final products for each of the mass relations used.

Experimental Part.

The work on the study of this problem has divided itself into two parts. The first division of the work, intended to be entirely preliminary in nature, has included the initial experimental work which was necessary in determining the conditions under which the equilibrium could best be studied. Also in the preliminary part of the work, the presence of the equilibrium or series of equilibria was definitely confirmed. The second division of the problem was concerned with the determination of the proportions of the final products as obtained from the equilibria under different conditions. The materials used in this part of the work were carefully purified and the greatest care was exercised in the separation and estimation of the different products.

Preliminary Work.

The conditions under which the experiment was studied: This
work consisted in determining by cut and try methods, the mass
relations, the time and temperature of heating, and the other
factors in the procedure, which would be most satisfactory for the
experiment. Radzuwanski[13], in his work on the ethyl benzene syn-
thesis, recommended that the temperature be kept as low as possible
and the experiment be run for a correspondingly long period of time.
He found that by maintaining the temperature at 7°C. it required
from 24 to 48 hours to complete the experiment. On the other
hand in the synthetic work at the Illinois laboratory, it has
been customary to heat the reacting materials to boiling, and keep
them at this temperature for a period of from one to three hours.
In order to compare these methods two runs were made using the
same masses and varying only the temperature and time of heating.
From these results it was found that the best yield was obtained
when the reaction was kept at a boiling temperature, for three
hours. Goldschmidt and Larson[14], in their study of the Friedel and
Crafts' reaction, passed hydrochloric acid gas into the mixture
during the time of heating, but from two experiments carried out
under these conditions in the laboratory, its application in this
work did not seem advisable. The amount of aluminium chloride to
be used was also determined as the result of several experiments,
which demonstrated that fifteen grams was sufficient to bring
about equilibrium with the reacting materials used in the propor-
tions of this experiment.

Proof of the Presence of an Equilibrium: In determining the

(14) Goldschmidt and Larson. Zeit. Phys. Chem. 48: 430 (1904)

presence of the equilibrium, it was decided that, for the pre-
liminary work, the proportion of the final products in the different
runs might be estimated with sufficient accuracy, by comparing the
corresponding fractions, which had been taken under equivalent
conditions; that is, through the same range of temperature, use of
the same distilling bulb and fractionating column, and redistilled
for the same number of times.

The products taken from two of the preliminary experiments
mentioned above, were poured together, 15 grams of aluminium
chloride added, and the reacting materials refluxed for three
hours at a temperature of 87°-$90^{\circ}C$. At the end of this time the
contents of the flask were cooled to 20° or less, and the mixture
poured into ice water contained in a separatory funnel. After
shaking well to remove all of the aluminium chloride, the upper
layer was dried slightly over calcium chloride, and then fraction-
ated. The fractionation was made from a one liter Ladenburg
distilling flask, having a four bulb column, and all fractions
were distilled and re-fractionated for the second time. The pro-
portions recovered are as given in Column I of the following
table.

TABLE I.

	I	II	III	IV	V
80° - 100°	396 cc	348 cc	165 cc	305 cc	280 cc
100 - 130	45	45	28	30	27
130 - 140	112	100	68	85	78
140 -	31	40	60	42	35
	584	533	321	462	420

In column II the products of I were poured together and

given a second application of aluminium chloride, in order to make
sure that the equilibrum had been reached. The fractions ob-
tained are those indicated in the second column. In the next
experiment, half of the 80°-100° and 100° - 130° fractions were
withheld and the equilibrium was shifted to the proportions of
column III. In Column IV are represented the fractions obtained
upon adding again the portions previously withheld and treating
with 15 grams of aluminium chloride for the usual three-hour
heating. This represents the original equilibrium proportions
of the reaction, but in order to further verify this, the frac-
tions were poured together once more and given another applica-
tion of aluminium chloride. The fractions obtained are given
in column V. It is to be observed that in each of the different
runs there is an evident loss, due to the manipulation. However,
for the sake of comparison, these products may be represented in
per cent of the total distillate from each run, giving the
figures of the following table.

TABLE II.

	I	II	III	IV	V
80° - 100°	67.0%	62.2%	51.4%	66.2%	66.6%
100 - 130	7.7	8.4	8.7	6.5	6.4
130 - 140	19.2	18.7	21.2	18.4	18.6
140 -	5.3	7.5	18.7	9.1	8.4

From these figures it is evident that there is an equilib-
rium present, for the proportions of the final products are shift-
ed by varying one of the factors, but when all these same factors
are held constant the proportion between the final products does
not change.

Chlorobenzene in the 130^0 - 140^0 fraction:

The presence of chlorobenzene was suspected as a possible result of the action of the aluminium chloride upon the benzene, and for that reason a quantitative determination was made upon the 130 -140^0 fraction. The method used was that of fusion with sodium peroxide in the Parr Peroxide bomb and gravimetric estimation of the chloride. The results of the analysis showed that the compound was present only in small amount, the average proportion of chlorobenzene in the fraction amounting to only 1.06 per cent. This amount is relatively small if we consider the fact that the product had been used in at least ten reactions.

Final Work.

Purification of the Materials:

The ethyl benzene and benzene used in determining the final data were carefully purified. The ethyl benzene, which was the product prepared by the students using the Wurtz Fitting synthesis was at first fractionated from an ordinary distilling bulb over a five degree range. To remove any halogen which might be present, the product was placed in a round bottomed flask with an equal amount of dry ether, and, after treating with 50 grams of sodium, 25 grams of ethyl bromide were added and the mixture allowed to stand for 24 hours. Then, after pouring off all of the sodium residues, the product was washed with water, and dried by allowing it to stand over night with calcium chloride. For the fractionation, the F. D.Brown constant temperature still-head was used. This column consists of four bulbs fitted up with small syphon tubes which return back the condensed vapor, while

mounted at the top is a test tube with a reflux condenser. In this test tube is placed a small quantity of a liquid which boils at the temperature at which the desired fraction is to be taken. By the use of this column it was possible to obtain as a final product, a fraction of ethyl benzene which boiled within a range of one-half of a degree.

The benzene used in this experiment was the special thiophene free product, and it, too, was redistilled and closely fractionated by the use of the Brown column. The benzene was tested according to the Standard tests of Purity as given by Merck, and gave satis- factory results for every test.

Method of Study and General Procedure:

In general the method of studying the reaction was the same as outlined in the preliminary work, except that it was chosen to keep the benzene concentration constant, and vary only the amount of the active ethyl radicle. Starting with the reacting materials in the ratio of ten moles of benzene to one mole of ethyl, a series of experiments were made using two, three, four, five and six moles of ethyl. As in the preliminary work, the materials were treated with 15 grams of aluminium chloride and kept at boiling temperature for three hours. They were then poured into ice water in a separatory funnel, and, after shaking thoroughly to remove all of the aluminium chloride, the benzene layer was separated and dried over calcium chloride. In order to recover any of the hydrocarbons which might be held in suspension in the aqueous layer, the wash water was placed in a distilling bulb and the first part of the distillate, which contained most of the suspended hydrocarbons, was saved.

This was then added to the benzene layer from which the final products were fractionated, the benzene and the ethyl benzene being separated and closely fractionated by means of the Brown column. The fraction boiling above 140° was placed into a smaller distilling bulb, and the di- and tri- ethyl benzenes were estimated after repeated fractionation. The three di-ethyl benzenes boil within close range of each other, between 181° and 185°, while the symetrical tri-ethyl benzene has its boiling point at 217°.

Each of the runs in the final work was made by the procedure outlined above, and the following results were obtained:

REACTING MATERIALS	FINAL PRODUCTS.	
(a)		
Ratio- 10 moles benzene to 1 mol ethyl.	Benzene	702 gr.
Using 9 moles of benzene (702 gr.) and	Ethyl benzene	81.7 "
1 mol of ethyl benzene (106 gr.)	Di-ethyl "	4.3 "
	Tri- "	0.0
(b)		
Ratio- 10 moles benzene to 2 moles ethyl	Benzene	619.9 "
Using 8 moles benzene (624 gr.) and	Ethyl benzene	186.8 "
2 mole ethyl benzene (212 gr.)	Di-ethyl "	10.2 "
	Tri "	0.6 "
(c)		
Ratio-10 moles benzene to 3 moles ethyl	Benzene	532.0 "
Using 7 moles of benzene (546 gr.) and	Ethyl benzene	307.0 "
3 moles of ethyl benzene (318 gr.)	Di- " "	19.7 "
	Tri- " "	1.8 "
(d)		

(Note: Half quantities were used in this experiment and all results are multiplied by two.)

Ratio-10 mol. benzene to 4 mol. ethyl	Benzene	466.0 "
Using 6 moles benzene (468 gr.) and	Ethyl benzene	377.4 "
4 moles ethyl benzene (424 gr.)	Di-ethyl "	33.2 "
(Multiplied by 2)	Tri- " "	2.2 "

(d')

To the fractions from (d) ten moles extra benzene were added, so that with the reacting materials in the same proportions as in

experiment (b), a check might be made on the results there obtained. Due to the fact that half quantities were used, the actual masses of both experiments are identical; that is, the 16 moles of benzene and 4 moles of ethyl benzene in half quantities amounted to the 8 moles benzene and 2 moles ethyl benzene used in experiment (b).

	Results of Exp. (d')		Results of Exp. (b)
Benzene	640.8 grams	Benzene	619.9 gr.
Ethyl Benzene	184.4 "	Ethyl Benzene	186.8 "
Di-ethyl "	11.2 "	Di-ethyl "	10.2 "
Tri " "	.6 "	Tri- " "	.6 "

The close check obtained would indicate that in each experiment the equilibrium stage had been attained. Half quantities were used on both of the remaining experiments.

(e)
Ratio of 10 mol. benzene to 5 mol. ethyl
Using 5 mol. (390 gr.) benzene and
5 mol. ethyl benzene (530 gr.)

Benzene	372	gr.
Ethyl benzene	350	"
Di- " "	78	"
Tri " "	20	"

(f)
Ratio-10 mol. benzene to 6 mol. ethyl
Using 4 mol. benzene (312 gr.) and
6 mol. ethyl benzene (672 gr.)

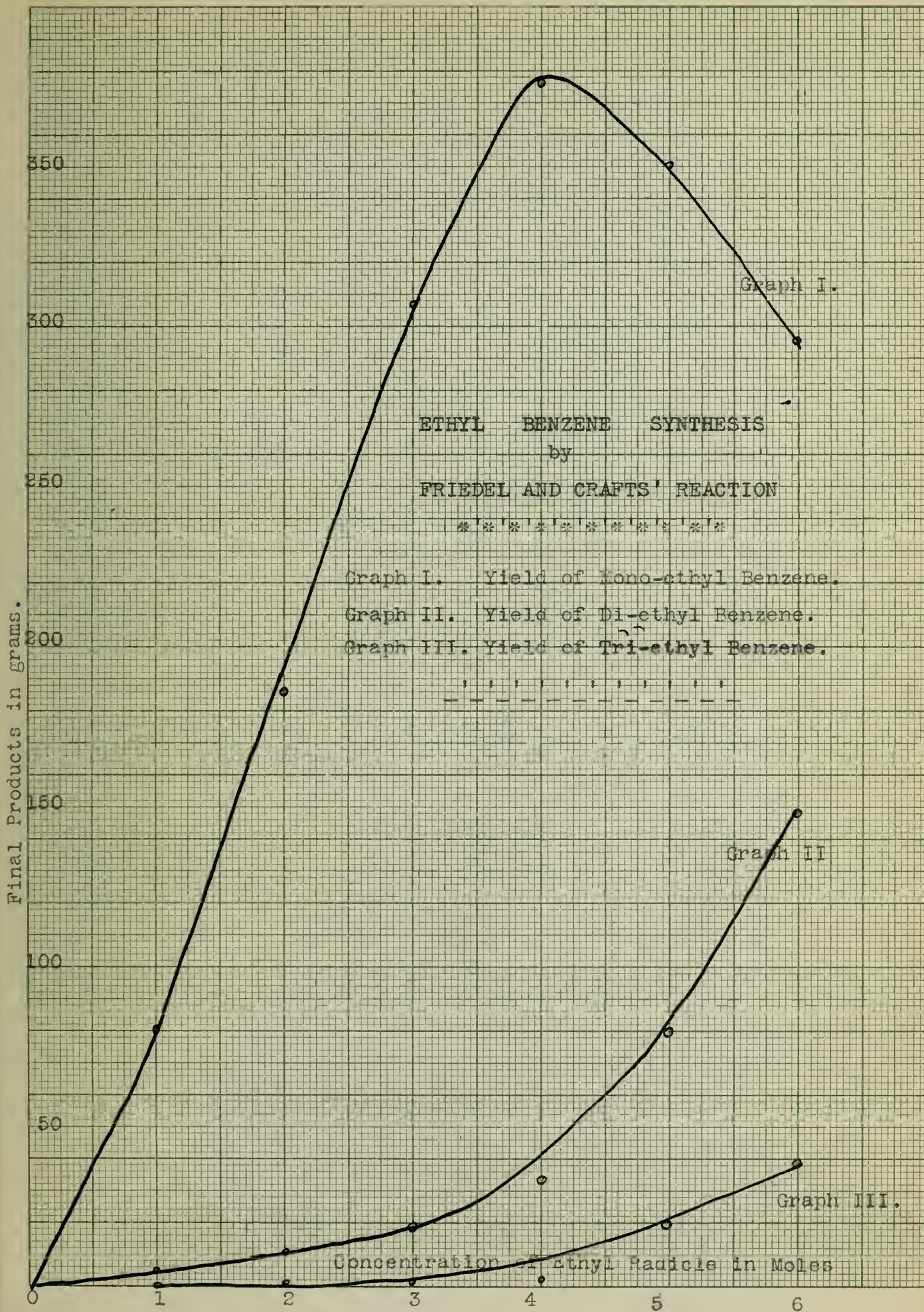| Benzene	457.0	"
Ethyl benzene	297.0	"
Di- " "	148.0	"
Tri-" "	38.5	"

Conclusions: Summary of Part III.

1. It has been shown that in the Friedel and Crafts' reaction there is a definite equilibrium or series of equilibria between the reacting materials.

2. This equilibrium has been studied in the case of the ethyl benzene synthesis by varying the concentration of the ethyl radicle, at the same time, holding constant all of the other factors of the reaction. From the data obtained in these
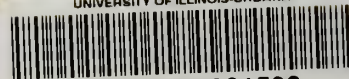
experiments, it is now possible to predict the amounts of the mono-
di-, and tri-ethyl benzenes formed under any given concentrations.
The factors which have been held constant throughout the series of
experiments are:

<div style="text-align:center">

Concentration of benzene   =   10 moles

Amount of Aluminium chloride =   15 grams

Time of heating   =   3 hours

</div>

  The data obtained is presented here in the form of three
graphs in which the final products in grams is plotted against
the concentration in moles of the ethyl group.

ETHYL BENZENE SYNTHESIS
by
FRIEDEL AND CRAFTS' REACTION

Graph I.   Yield of Mono-ethyl Benzene.
Graph II. Yield of Di-ethyl Benzene.
Graph III. Yield of Tri-ethyl Benzene.